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Petr Vanýsek
Northern Illinois University
Department of Chemistry
DeKalb, IL 60115
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Charge transfer processes on liquid/liquid interfaces:
The status in 1994

Petr Vanýsek

Northern Illinois University, Department of Chemistry

DeKalb, IL 60115–2862 (U.S.A.)

ABSTRACT

Electrochemistry dealing with interfaces between two immiscible and ionically conductive solutions (ITIES) has been documented in literature already a hundred years ago. The work has only recently attracted a wider attention, with more modern treatment founded by the late Professor Jiří Koryta. The principle of the work, its past and new trends in experimental electrochemistry, optical studies of the interface and recently emerging theoretical work are reviewed.

The thermodynamically grounded interest in electrified interfaces is now just over a century old and it closely follows establishment of physical chemistry as an individual scientific discipline. Its first specialized journal, the Zeitschrift für physikalische Chemie, founded in 1887 by Wilhelm Ostwald, was in its early years devoted mainly to electrochemical research. There, in 1988 the derivation of the

Nernst equation appears [1], which can be applied not only to metal/solution interfaces, but to the liquid/liquid interfaces as well.

Systematic study of charge transport across immiscible interfaces and its implications to electrochemistry and electroanalysis as a separate discipline is relatively young. Its beginning could be placed approximately to middle 1970's. At first a research subject of only a few groups, it recently became a study project of quite a few individuals. In fact, a number of symposia devoted to this subject took place or are planned, such as those held at the Electrochemical Society meetings in spring 1987 (Philadelphia), fall 1992 (Toronto), and spring 1995 (Reno), or the May 1994 Heyrovský Discussion "Electrochemical Processes on Liquid Membranes" in Třešt, Czech Republic. This review highlights recent developments and emphasizes non–traditional or unusual applications of the studies in liquid/liquid electrochemistry.

It was the original paper by Koryta *et al.* [2] from 1976 that spurred the present interest in the electrochemical behavior of the interface between two immiscible electrolyte solutions (ITIES[1]). The paper pursued experimentally the idea that the liquid/liquid interface could serve as a model for a half of a simplified biological membrane. The similarity with a biological membrane surface has been noted however much earlier, in 1848 by Du Bois–Reymond [3], who then suggested that the surfaces of biological systems have properties similar to those of an electrode of a galvanic cell.

Koryta's research [2] lead to the realization that description of transport

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[1]It was Koryta who coined the acronym ITIES. Some consider it funny, when pronounced in English as "i–tees". In Czech, though, without much consternation, this acronym is pronounced as English letters E–T–S.

across ITIES resembles in many ways description of redox processes on electrode surfaces. The parallelism of the ion transport through a liquid/liquid interface and an ion transport to an electrode surface is both advantage and disadvantage for understanding the concept of the ITIES. Experimental techniques, their principles and descriptive mathematics already known for redox studies are usually applicable to ITIES. However, although the processes on the interfaces are principally simple, they are not intuitively obvious and the ITIES studies do not enjoy a broad attention although the implications of its research are far reaching.

The work of Nernst [1] and Planck [4] from 1888–1890 mark the first important progress on transport in electrolyte solutions. The thermodynamics of the liquid/liquid interface at equilibrium leads to relationships that resemble the Nernst equation for electrodes in solutions. In a system of immiscible solutions (oil/water) in contact that contain such ideal dissociated salts that both phases share only a single ion i, the interfacial potential can be described by relationship:

$$\Delta\varphi_{oil}^{water} = \Delta\varphi^{o}{}_{oil}^{water} + \frac{RT}{Fz}\ln\frac{a_i^{oil}}{a_i^{water}} \tag{1}$$

where $\Delta\varphi^{o}{}_{oil}^{water}$ is the standard potential of transfer of ion i from water to an oil phase, a_i is the activity of the shared ion in the designated solvent, and z is signed charge of the ion.

The first original experiment on ITIES, polarization of water–phenol interface [5], was performed in 1902. In that experiment it was transport of iodide (in potassium iodide) that was observed. Until 1960's there were only a few papers related to, but not directly addressing, the topic of electrochemistry of ITIES. That has gradually changed until recent years, when the number of papers related to ITIES has peaked at 91 in 1990 (Fig. 1). The graph is informative, although likely imprecise. The counted publications include papers known to the author and

deemed by him to be related to ITIES. The low value for 1994 can easily be explained by the fact that only 8 months of the year are covered. Also, some literature becomes known to be pertinent to the ITIES subject only a few years after its publication. Nevertheless, some decrease in the volume of publications is real. The dashed line in Fig. 1 shows the publications on L/L subject as they were known in 1992. The relative decrease observed for 91 has not been quite rectified, although 75 publications were documented for that year in late 1994, compared to 58, known in 1992. The fluctuations in publication activity are caused by the fact that only several groups participate in the project and publication of new results is not a process evenly distributed in time.

Systematic research on ITIES is limited to several groups throughout the world. The countries in which some work on liquid–liquid interfaces has been done are Argentina, China, Czech Republic, Ethiopia, Finland, France, Germany, Holland, Italy, Japan, Mexico, Poland, Portugal, Russia, Switzerland, United Kingdom and the USA. At current time Japan leads with about six groups actively involved in ITIES. The interest in ITIES in the USA is only recent and relatively small.

The topics that are relevant to the study of ITIES and most of which are included in the data of Fig. 1 are: 1. single ion partition theory; 2. double layer structures; 3. double layer potential profiles in relation to kinetics of single–ion transfer; 4. unusual diffusion properties in mixed layers of solvent between two immiscible phases; 5. charge transfer kinetics; 6. redox electron transfer across ITIES; 7. ionophore/charge carrier/complex induced or sustained ion transport; 8. ITIES related to transport in lipid bilayers and biological structures and physiological studies; 9. ITIES related to behavior of chemical microdomains; 10. electrolyte/ion–exchanger charge transport; 11. surface phenomena of ITIES; 12.

design and construction of chemical sensors; 13. ion exchange chromatography; 14. power sources with nonaqueous electrolytes; 15. phase transfer catalysis and 16. instrumentation used or usable in ITIES studies.

Introduction to the technique

The electrochemistry of ITIES invokes a concept that is quite simple, even though not intuitively obvious. Actually, because the voltammetric response of the ITIES resembles so much the response of a metal electrode/solution interface, although no electron transfer reaction at ITIES is even occurring, the obtained cyclic voltammograms can be sometimes confusing.

The concept of the ITIES experiments can be explained on cyclic voltammetry. The interface in most experimental situations consists a horizontal boundary, that arises between two immiscible liquids of different densities such as water and nitrobenzene.

The diagram of the voltammetric cell is shown in Fig. 2. The cell is connected with two reference (RE_1 and RE_2) electrodes and two counter platinum electrodes (CE_1 and CE_2) to a special four—electrode potentiostat with differential reference electrode input. The potentiostat maintains desired potential between the tips of the reference electrodes, placed in the vicinity of the interface. It is possible to polarize the interface with a voltage program appropriate for voltammetry.

A voltammogram obtained for typical supporting electrolytes [6] is shown in Fig. 3, curve *A*. The usual supporting electrolytes are LiCl solution in the aqueous phase and tetrabutylammonium tetraphenylborate (TBATPB) in the nitrobenzene phase. Because LiCl is a hydrophilic salt, Li^+ and Cl^- ions will

remain confined mostly in the aqueous phase. Similarly, TBATPB dissociates in nitrobenzene, but its respective ions TBA^+ and TPB^- remain almost exclusively in the nitrobenzene phase. Thus, an interface between two ionically conductive, but immiscible phases, is formed. Such an interface, as long as it does not pass charge carriers, can be polarized to a desired potential value and behaves as an ideally polarizable interface. The sign convention on ITIES is such that the aqueous phase is most positive at the right extreme of the voltammogram. The onset of the currents limiting the supporting electrolyte working range are due to the supporting electrolyte ions transport into phases in which they are normally absent. The current of the right extreme is caused by crossing of tetraphenylborate anion from nitrobenzene to water, and Li^+ in the opposite direction. The left limit is caused by Cl^- crossing from water into nitrobenzene and tetrabutylammonium cation crossing in the reverse direction. In the middle of the potential window only a charging current corresponding to the double–layer region is observed. This range of potentials in which no significant transport of supporting electrolytes takes place is suitable for studies of semihydrophobic ions, such as tetramethylammonium cation ($TMeA^+$) in the following example.

Curve B in Fig. 3 results from addition of 0.47 mmol/l of $TMeA^+$ in the aqueous phase. If the aqueous phase is made more positive by scanning to the right, a transport of the $TMeA^+$ cation into nitrobenzene will occur. Upon reversing the scan at the right extreme, the transport of $TMeA^+$ from nitrobenzene back to water is observed.

The transport across the interface is by all indications diffusion controlled and therefore the voltammetric curves and equations describing them are similar to those for transport of oxidizable species to an electrode and transport of the oxidized product away from the electrode. Therefore, the voltammograms for both

processes have similar features, e.g., a separation of the positive and negative peak potentials by 58/n mV for a reversible process.

The voltammetric curves can be used for analytical as well as mechanistic studies. The position of the peaks is a function of the Gibbs energy of transfer (or the standard potential of transfer ($\Delta \varphi^o {}^{water}_{oil}$) of the particular ion and it can be used for qualitative analysis. Quantity can be determined from the height of the peaks. The current measured at the peak of the curve (i_p) is given by

$$i_p = 269 \, c^o \, n^{3/2} \, A \, D^{1/2} \, v^{1/2} \, . \tag{2}$$

The current will be in amperes if the scan rate v is expressed in V/s, the interface area A in cm^2, the diffusion coefficient D in $cm^2 s^{-1}$ and the bulk analyte concentration c^o mol/l. The n is charge of the transported ion.

New developments

Early works on ITIES have drawn from the experience of polarography and have lead to the construction of an electrolyte dropping electrode with voltage scan. The current scan approach is now more popular [7,8]. Further studies utilize cyclic voltammetry and chronopotentiometry. Many new techniques of electrode electrochemistry have been adopted for ITIES studies, with such examples as impedance spectroscopy, electrocapillary techniques and most recently, in parallel with ultramicroelectrodes, the utilization of a microinterface between two immiscible liquids.

The purpose of using a small orifice separating two immiscible electrolytes is the same as is the purpose of ultramicroelectrodes; to lower or eliminate the effect of *IR* drop in the solutions. This is made possible because the diffusion towards the interface is hemispheric rather than semilinear. Small interfaces have

been used by Girault and coworkers [9–12] and by Senda [13]. One complication that makes the experiment challenging is the actual process of restricting the area of the interface. Some of the work was done on a small blunt capillary tip. To take full advantage of the hemispheric diffusion in both solutions, the microinterface has to be made in a thin flat separator. Girault perfected the formation of a microITIES by photoablation. Focused UV light causes breakage of bonds in a polyester film that can be later dissolved. Smallest diameter so far achieved was 5 μm. Others used in forming a microITIES a hole in a thin glass wall [14]. An alternative that makes the interface more rigid is to solidify one phase by a gel, such as PVC in the case of nonaqueous nitrobenzene solution [15]. The microinterface which has inherently high resistance, is an excellent source of electrochemical noise that can be used for impedance measurements without the need for outside perturbing signal [16–18].

Three schools of thought regarding the structure of the interfacial double layer are represented by H. H. Girault, T. Kakiuchi and Th. Wandlowski [19]. The main differences and concerns, that still need to be resolved, are the appearance of the boundary, in particular whether the boundary can be perceived as a sharp border or whether it is smeared out, over several molecular lengths. Other problem noted in the effort aimed to establish the apparent kinetic constants of charge transfer on L/L interfaces is the dist··rbing observation that the reported values of rate constants for a given system seem to be increasing with the year of publication [20]. This noted irreproducibility is likely caused by the relatively large interface capacitance that could have obscures the actual rates, especially in the early years of the L/L work [21].

The ITIES also has caught attention of some theorists and workers in fields allied to electrochemistry using some combined techniques. Light was used in

detection of the movement of the interface [22], in monitoring concentration gradient changes using probe beam deflection method [23], in fluorescence quenching upon dye transport from one phase to another [24], in analytical voltfluorometry [25, 26] and it was also directly used to investigate photoelectric effects on ITIES [27–31]. Second harmonic generation on L/L interface [32–36] can provide non–electrochemically information about the state of the interface as long as molecules that yield the second harmonic signal can be preferentially accumulated at the interface. Higgins and Corn [32] used their method of second harmonic generation on surfaces to learn about molecules adsorbed at electrically polarized interface between water and 1,2–dichloroethane. Janata and Bruckner–Lea [37] describe what they call the molecular vice — a device in which a surface area of a drop is decreased to form an oriented interfacial layer. Tunneling microscopy then can be used at the liquid/liquid interfaces. ITIES provide still a strong foundation for electroanalytical purposes in sensor and transducer development [19, 38–42].

We have used the quartz crystal microbalance (QCMB) to observe changes at the water/nitrobenzene interface. The gold plated 5 MHz crystal had its exposed side covered by a thin layer of electrodeposited polyallylphenol. The purpose of this coating was to prevent an electric contact and short–circuiting the two phases in contact. The crystal was immersed through the interface vertically (Fig. 4), intersecting thus the L/L boundary at a single line (inset). The interface was polarized by a voltammetric sweep and both the resulting current and the QCMB frequency were recorded as a function of the applied potential. Figure 5 shows the result for an interface formed between water/nitrobenzene, containing only the supporting electrolytes, LiCl and tetrabutylammonium tetraphenylborate. The observed effect is a result of two effects combined: The change in the

interfacial tension as a function of applied potential and second, formation of a precipitate due to transport of the supporting electrolyte ions in the solvent in which they are inherently insoluble. So far only qualitative data showing how the QCMB frequency is following the voltammetric curves, are available.

The L/L interfaces recently also attracted high caliber instrumentation methods. Eisenthal [43] describes fast laser methods to learn about the structure of the interfaces. Cosgrove et al. [44–45] used neutron scattering for a L/L interface to study interfacial adsorption. Als–Nielsen and Freund [46] describe experimental arrangements on a synchrotron UV source for liquid surface studies. This work is also consistent with our proposed studies [47].

Information about interfacial structure of ITIES is also important in theoretical work in ITIES. Marcus [48–49] derived relationship for electron transfer across ITIES. He used the experimental data of Geblewicz and Schiffrin [50] to derive relationships describing electron transport on ITIES. This work fills a gap between theoretical prediction and an experiment. To decide between two models proposed by Marcus, more experimental data on electron transfer across ITIES, which are so far quite rare, are needed.

Recent years attracted theorists to apply their skills to ITIES. Molecular dynamics calculations on ITIES were done as well as was performed modeling of surfactant absorption on liquid/liquid interfaces. Benjamin [51–54] used computer methods to model ion transfer across the liquid/liquid interface. Smit used computer simulation to model a water/oil interface in presence of micelles [55–56], and for surfactant adsorption [57]. Hayoun et al. in a similar fashion evaluated a solute–transfer reaction across the interface [58]. In the past years a work from several new groups has appeared, for example in Finland [59], at Chiba University, Japan [60–61] and Hebei University, China [62]. Interesting from chemical point of

view and new to the ITIES studies are heteropolyanions (polytungstate, poly-molybdate). Their transport across L/L interface was reported recently [63–65].

Acknowledgment

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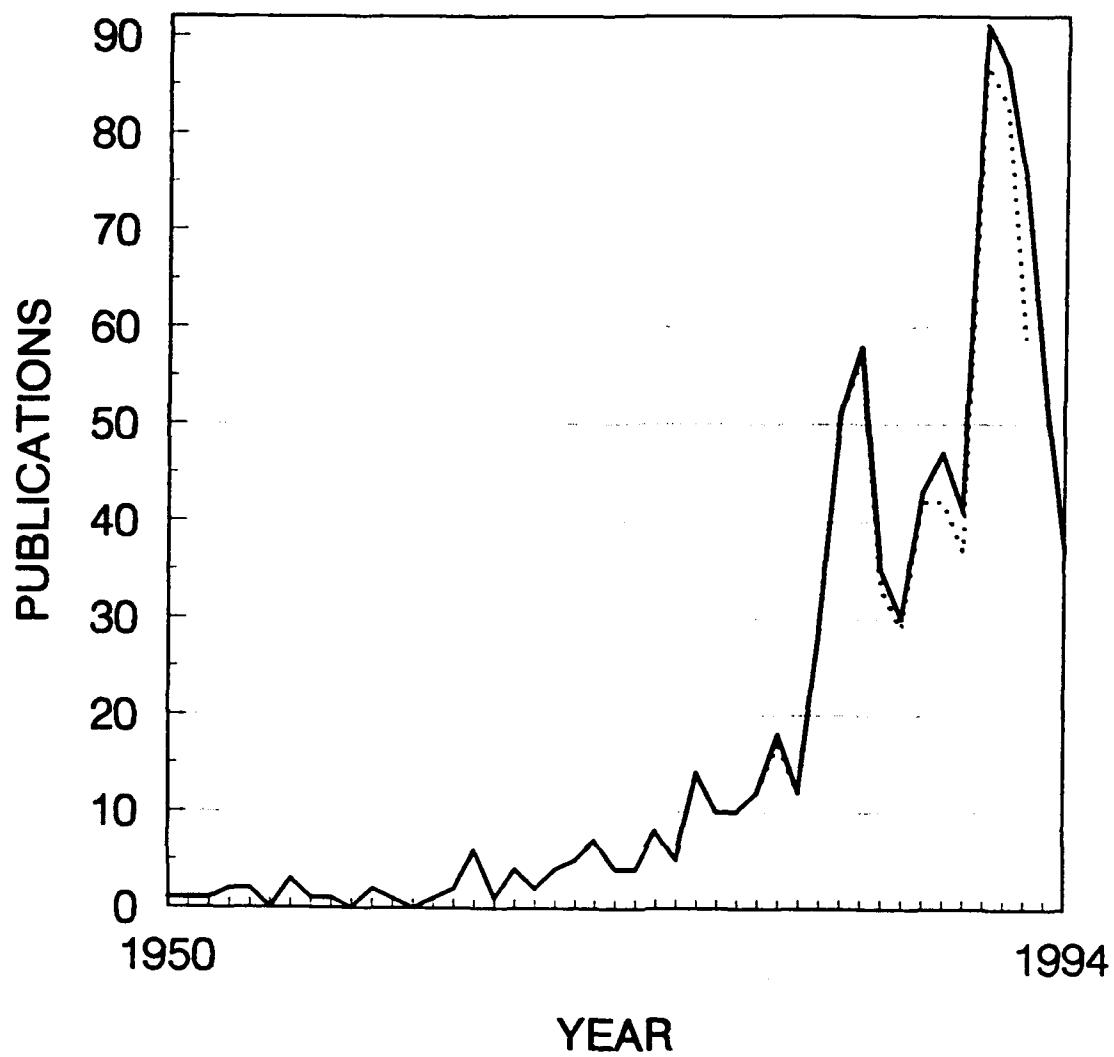
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List of figures:

Fig. 1

Fig. 2

TMeA$^+$(aq) $\longrightarrow$ TMeA$^+$(nb)

TMeA$^+$(nb) $\longrightarrow$ TMeA$^+$ (aq)

Fig 3

insulator

Au

QUARTZ

water phase
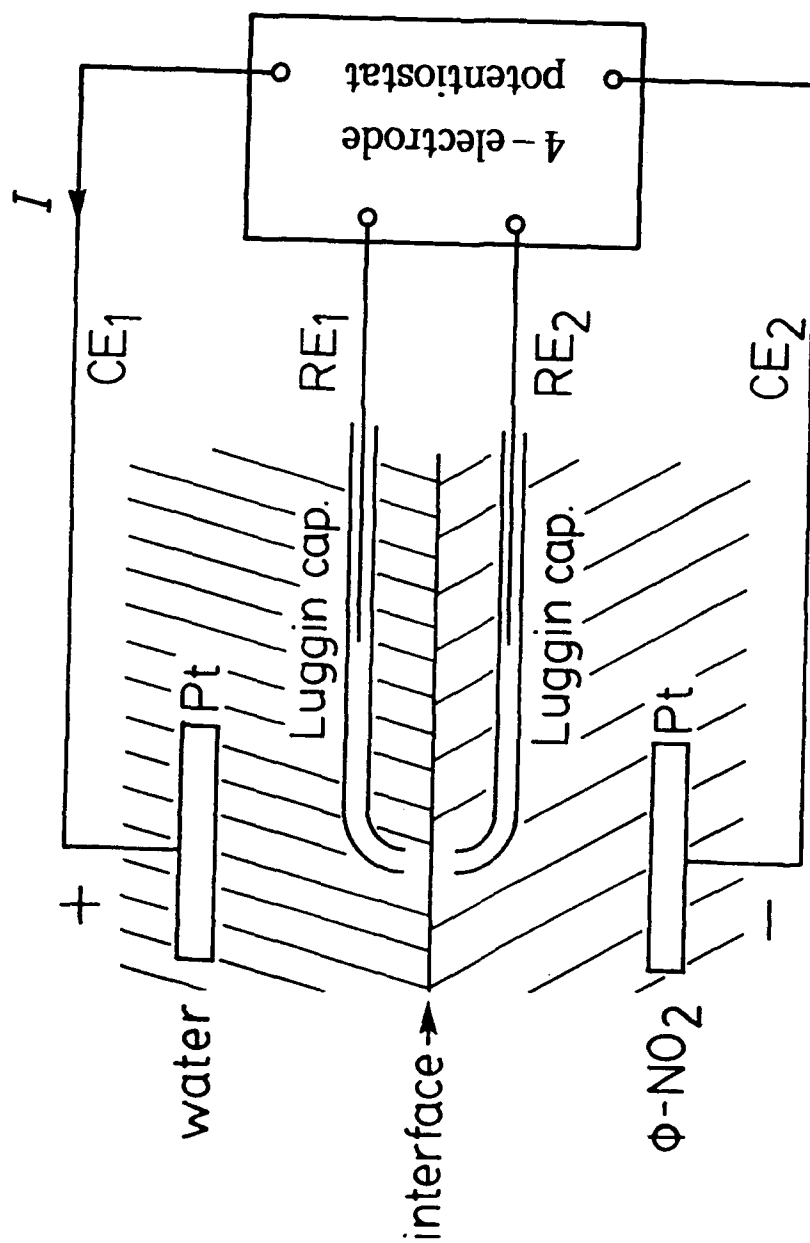
+

nonaqueous phase

−

precipitate

crystal

H_2O

NB

Fig 4

Фиг 5
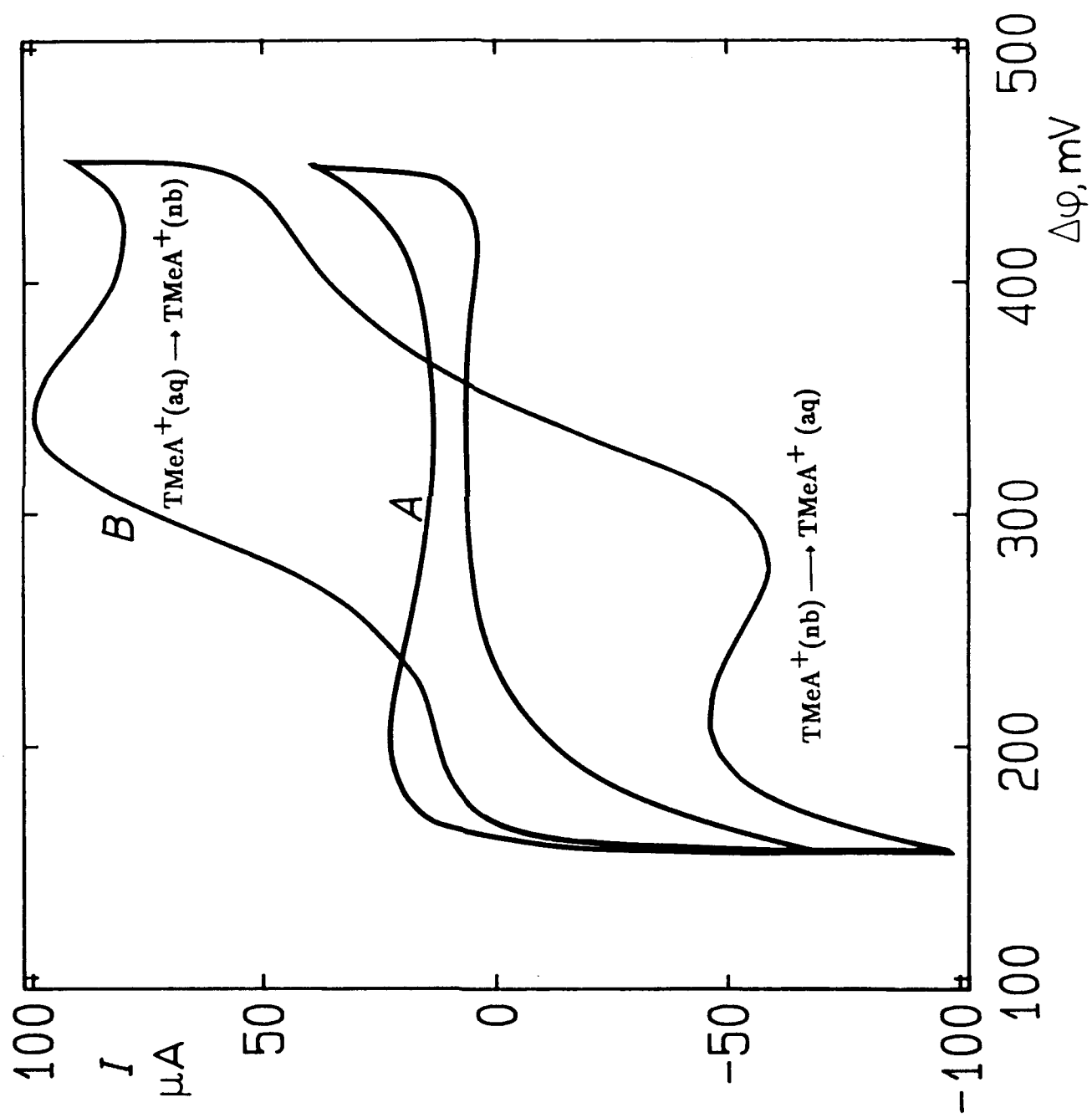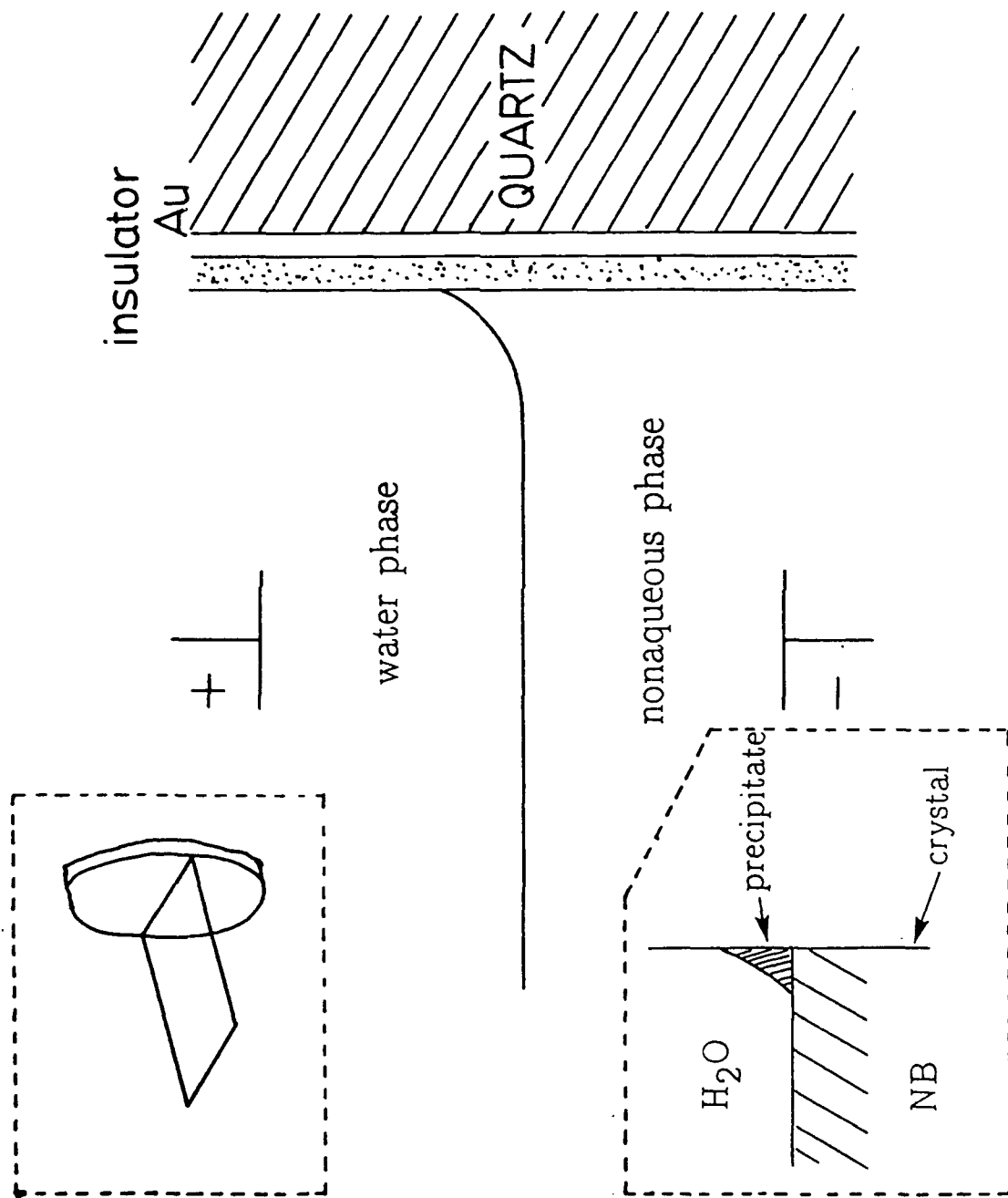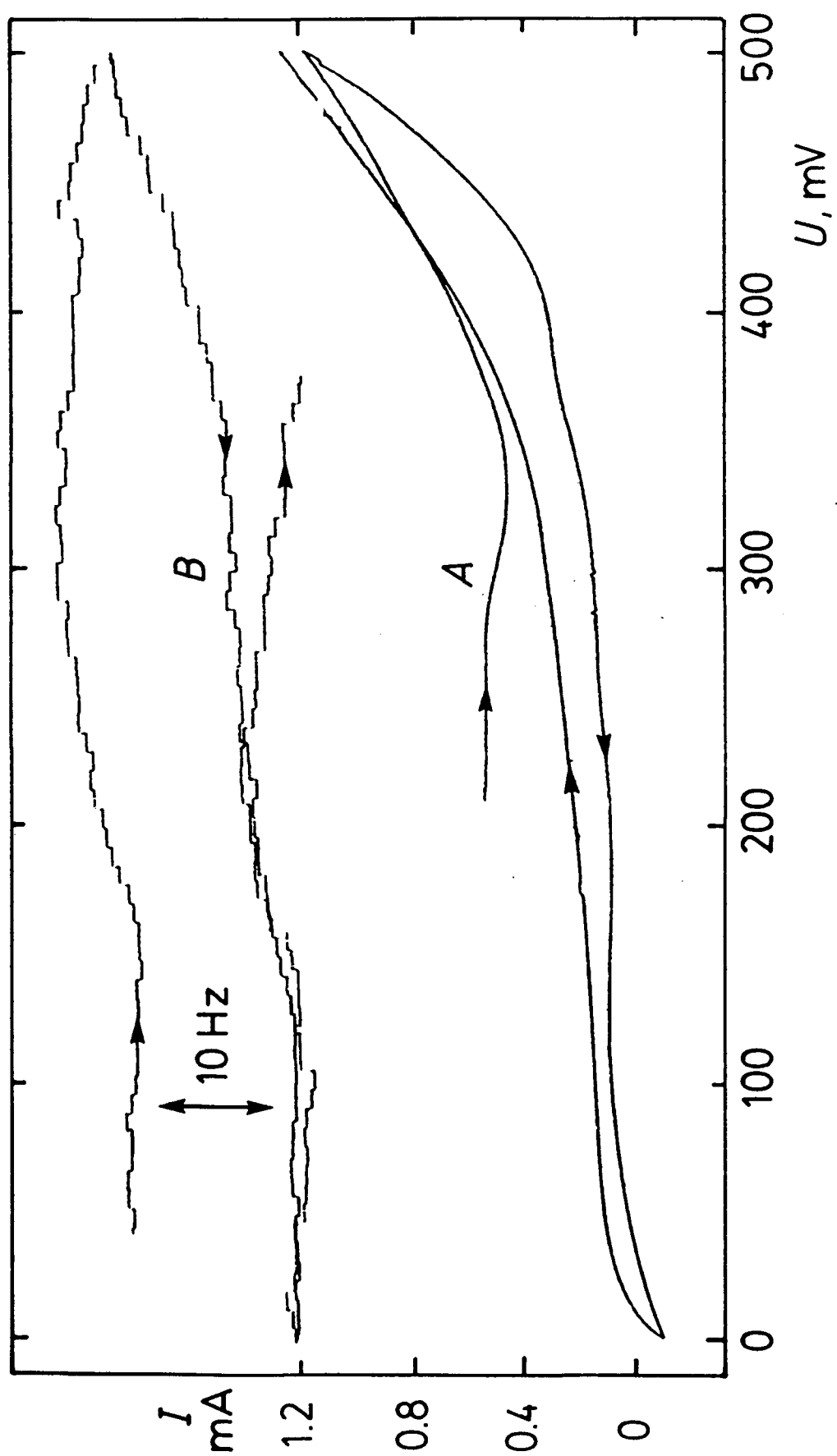
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